# This Page Is Inserted by IFW Operations and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

## (12) UK Patent Application (19) GB (11) 2 293 795 (13) A

(43) Date of A Publication 10.04.1996

- (21) Application No 9519924.6
- (22) Date of Filing 29.09.1995
- (30) Priority Data
  - (31) 06235160
- (32) 29.09.1994
- ).1994 (33) JP
- (71) Applicant(s)

**NEC Corporation** 

(Incorporated in Japan)

7-1, Shiba 5-Chome, Minato-Ku, Tokyo, Japan

- (72) Inventor(s)
  Hiroshi Ogawa
- (74) Agent and/or Address for Service

  Mathys & Squire

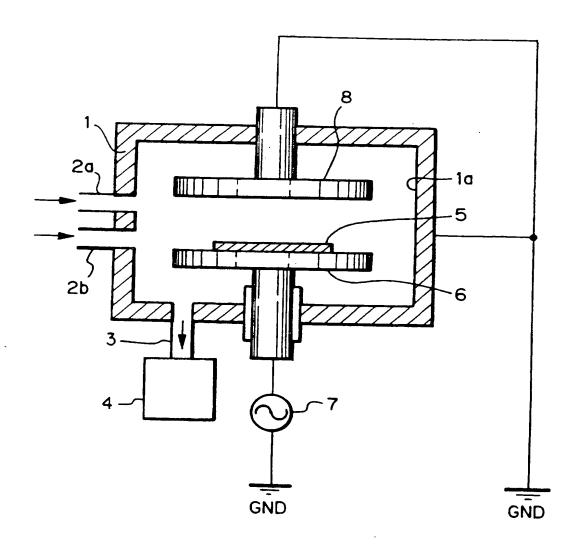
  100 Grays Inn Road, LONDON, WC1X 8AL,
  United Kingdom

- (51) INT CL<sup>6</sup>
  C23C 16/44 , C23G 5/00
- (52) UK CL (Edition O ) **B6J** JMB1 J501 J70X **U1S** S2061
- (56) Documents Cited
  WPI Abstract Accession No.86-335260/51 &
  JP61250185A (Nichiden Anelva)-see abstract
- 58) Field of Search UK CL (Edition N.) B6J JMB1 JMB2 JMB3 JMX JMY INT CL<sup>6</sup> C23C 16/44., C23G 5/00 ONLINE:WPI,CLAIMS

### (54) Cleaning vacuum processing chamber

(57) In a method for cleaning a vacuum process chamber of a dry etching apparatus, oxidative gas including rare gas is introduced into the vacuum process chamber and plasma is excited therein. Then, after the plasma oxidative gas is exhausted, fluoride gas is introduced into the vacuum processing chamber and plasma is excited therein.

Fig. 1



TO THE STATE OF TH

## METHOD FOR CLEANING VACUUM PROCESSING CHAMBER

BACKGROUND OF THE INVENTION Field of the Invention

The present invention relates to a method for cleaning a vacuum processing chamber of a dry etching apparatus for carrying out an etching process using bromide gas.

Description of the Related Art

A dry (plasma) etching apparatus has been broadly used in obtaining a fine structure of 10 semiconductor devices. In a dry etching method, a silicon substrate having a polycrystalline silicon layer deposited thereon is located within a vacuum processing chamber, and then, a hydrogen bromide (HBr) gas is introduced into the vacuum processing chamber. Then, plasma is excited to etch the polycrystalline silicon layer. In this plasma 15 etching, a residualreaction product such as silicon bromide (SixBr,) is deposited on to an inner wall of the vacuum processing chamber, electrodes, and the like. Such a residual reaction product deteriorates the etching characteristics. That is, a side etching process is 20 advanced, and the etching rate of polycrystalline silicon is fluctuated, so that reproducibility of etching cannot be obtained. Also, when air is introduced into the vacuum processing chamber, the water component thereof is reacted 25 with the residual reaction product to generate strong hydrogen bromide gas. Therefore, it is necessary to clean the residual reaction product in the vacuum chamber.

In the prior art, no method for cleaning the residual reaction product of Si<sub>x</sub>Br, has been suggested yet. Therefore, the residual reaction product of Si<sub>x</sub>Br, is manually scraped out. As a result, since the vacuum processing chamber cannot be successively operated, the efficiency is reduced. Also, this manual scraping operation is disadvantageous in respect of the safety of the

operators. Further, since the vacuum chamber and its peripheral equipment may be rusted, the manufacturing yield of semiconductor devices by using the vacuum processing chamber is reduced.

Note that JP-A-SHO61-250185 discloses a method for cleaning a residual reaction product of silicon chloride (Si \*Cl\*,) from a vacuum processing chamber. In JP-A-SHO61-250185, oxidative gas is introduced into the vacuum processing chamber and plasma is excited therein. Then, after the plasma oxidative gas is exhausted, fluoride gas is introduced into the vacuum processing

chamber and plasma is excited therein. Even if this cleaning method is applied to the residual reaction product of Si<sub>x</sub>Br<sub>y</sub>, it is impossible to homogeneously and affectively convert Si Br into silicon oxide. As a

effectively convert Si<sub>x</sub>Br, into silicon oxide. As a result, since Si<sub>x</sub>Br, hardly reacts with fluoride gas, Si<sub>x</sub>Br, is still left in the vacuum processing chamber.

Also, in JP-A-HEI2-138472, which discloses a method for cleaning residual silicon deposit in a vacuum processing chamber, use is made of plasma of a gas mixture of SF6, oxygen containing gas and rare gas. However, it is impossible to apply this cleaning method to the residual reaction product of Si<sub>x</sub>Br<sub>y</sub>.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new method for cleaning a vacuum processing chamber to remove residual reaction products such as SixBry.

According to the present invention, in a method for cleaning a vacuum process chamber of a dry etching apparatus, oxidative gas including rare gas is introduced into the vacuum process chamber and plasma is excited therein. Then, after the plasma oxidative gas is exhausted, fluoride gas is introduced into the vacuum processing chamber and plasma is excited therein. As a result, the bromine group of Si<sub>x</sub>Br, is replaced by oxygen in an oxidative plasma gas, to thereby create

5

10

20

25

silicon oxide (SiO<sub>2</sub>). In this case, the oxidative plasma gas is diluted by the rare gas, so that the oxidative plasma gas is homogeneously distributed within the vacuum processing chamber. Also, light emitted from the plasma of rare gas which has a line spectrum promotes the abovementioned replacement reaction. Thus, Si<sub>x</sub>Br, is completely converted into silicon oxide under an oxidative plasma gas including rare gas, and therefore, the silicon oxide is removed by the fluoride plasma gas.

10

15

#### BRIEF DESCRIPTION OF THE DRAWING

The present invention will be more clearly understood from the description as set forth below, with reference to the accompanying drawing, wherein:

Fig. 1 is a cross-sectional view illustrating a vacuum processing chamber to which an embodiment of the method for cleaning a residual reaction product of Si<sub>x</sub>Br<sub>y</sub> is applied.

20

30

35

## DESCRIPTION OF THE PREFERRED EMBODIMENT

In Fig. 1, reference numeral 1 designates a vacuum processing chamber of a dry etching apparatus. Provided in the vacuum processing chamber 1 are gas inlets 2a and 2b and a gas outlet 3. The gas outlet 3 leads to a vacuum exhaust system 4.

A semiconductor substrate 5 is mounted on a substrate holder 6 which also serves as an electrode which is connected to a high frequency power supply source 7. In this case, assume that a polycrystalline silicon layer is deposited on the semiconductor substrate 5 by a chemical vapor deposition (CVD) process in advance.

Also, reference numeral 8 designates a ground electrode. Note that the vacuum processing chamber 1 is also grounded.

A dry etching process for the polycrystalline silicon layer is now explained. That is, hydrogen bromide (HBr) is introduced via the gas inlet 2a into the vacuum

processing chamber 1, and the high frequency power supply source 7 is turned ON to excite plasma therein. As a result, bromine radicals and bromine ions are reacted with the polycrystalline silicon layer, and therefore, the polycrystalline silicon layer is converted into silicon bromide which is exhausted via the gas outlet 3 from the vacuum processing chamber 1. That is, the polycrystalline silicon is etched. In this case, silicon bromide is deposited onto an inner wall la of the vacuum processing chamber 1, the substrate holder 5, the ground electrode 8, and the like.

A cleaning method for the residual silicon bromide is explained next in detail.

First, oxygen including for example, helium (He) gas is introduced via the gas inlet 2b into the vacuum 15 processing chamber 1, and the high frequency power supply source 7 is turned ON to excite plasma therein. The conditions are preferably as follows:

> the mixture ratio of He to O2: 3:7 gas stream amount: 15 to 300 sccm gas pressure: 80 to 300 mTorr frequency of the source 7: 13.56 MHz power of the source 7: 100 to 1000 W.

As a result, the following reaction occurs:

 $SiBr_4 + He + O_2 \rightarrow SiO_2 + He \uparrow + 2Br_2 \uparrow \cdots (1)$ Note that, if the mixture ratio of He to O2 is smaller than approximately 10 percent, the strength of light emitted from the plasma helium may be so weak as to not excite the bromine group of SiBr4. On the other hand, if 30 the mixture ratio of He to O2 is larger than approximately 90 percent, the oxygen is generally so short as to not promote the above-reaction (1). Therefore, the mixture ratio of rare gas such as helium to oxygen is preferably within a range of approximately 10 to 90 percent.

Next, the introduction of the oxidative gas including helium is stopped, and an exhaust operation is performed upon the vacuum processing chamber 1.

10

20

25

35

Next, fluoride'gas such as sulfur hexafluoride gas is introduced via the gas inlet 2b into the vacuum processing chamber 1, and the high frequency power supply source 7 is turned ON to excite plasma therein. The conditious are preferably as follows:

gas stream amount : 15 to 300 sccm gas pressure: 80 to 300 mTorr frequency of the source 7: 13.56 MHz

power of the source 7: 100 to 1000 W.

10 As a result, the following reaction occurs:

 $SiO_2 + SF_6 \rightarrow SiF_4 \uparrow + SF_2 \uparrow + O_2 \uparrow \cdots$  (2)

Finally, the introduction of the fluoride gas is stopped, and an exhaust operation is performed upon for the vacuum processing chamber 1.

15 According to the experiments carried out by the inventor, after the above-described cleaning method is carried out, no smell of hydrogen bromide has been found, and no residual reaction product (Si<sub>x</sub>Br<sub>y</sub>) has been found in the inner wall of the vacuum processing chamber 1. A time required for cleaning the vacuum processing chamber and the electrodes was about 30 minutes, while a time required for manually scraping the residual reaction product(Si<sub>x</sub>Br<sub>y</sub>) was about 6 hours.

In the above-described embodiment, although
25 helium is used as the rare gas, other rare gases such as
neon (Ne), argon (Ar) and the like can be used. Also,
water (H<sub>2</sub>O), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or ozone (O<sub>3</sub>) can
be used as oxidative gas instead of oxygen. Further,
carbon tetrafluoride (CF<sub>4</sub>), nitrogen trifluoride (NF<sub>3</sub>), or
30 their mixture gas can be used as fluoride gas instead of
SF<sub>6</sub>.

As explained hereinbefore, according to the present invention, the residual reaction product(Si<sub>x</sub> Br<sub>y</sub>) can be homogeneously and effectively removed from the vacuum processing chamber, the electrodes, and the like.

Each feature disclosed in this specification (which term includes the claims) and/or shown in the drawings may be incorporated in the invention independently of other disclosed and/or illustrated features.

The appended abstract as filed herewith is included in the specification by reference.

#### CLAIMS

1. A method for cleaning a vacuum processing chamber for processing a silicon substrate with bromide gas, comprising the steps of:

introducing oxidative gas including rare gas into said vacuum processing chamber to excite plasma in said oxidative gas;

exhausting said oxidative gas from said vacuum processing chamber; and

introducing fluoride gas into said vacuum 10 processing gas to excite plasma in said fluoride gas, after exhausting said oxidative gas.

- 2. A method as set forth in claim 1, wherein said oxidative gas is one of  $O_2$  gas,  $H_2O$  gas,  $H_2O_2$  gas, and  $O_3$  gas.
- 3. A method as set forth in claim 1 or claim 2, wherein the mixture ratio of rare gas in said oxidative gas is approximately 10 to 90 percent, preferably 10 to 80 percent.
- 4. A method as set forth in any one of claims 1 to 3, wherein said rare gas is one of He gas, Ne gas and Ar gas.
- 5. A method as set forth in any one of claims 1 to 4, wherein said fluoride gas is one of NF<sub>3</sub> gas,  $C_2F_6$  gas,  $CF_4$  gas and  $SF_6$  gas.

Patents Act 1977 Examiner's report (The Search report	to the Comptroller under Section 17	Application number GB 9519924.6	
Relevant Technical Fields		Search Examiner R J MIRAMS	
(i) UK Cl (Ed.N)	B6J (JMB1, JMB2, JMB3, JMX, JMY)		
(ii) Int Cl (Ed.6)	C23C 16/44, C23G 5/00	Date of completion of Search 21 DECEMBER 1995	
Databases (see below) (i) UK Patent Office collections of GB, EP, WO and US patent specifications.		Documents considered relevant following a search in respect of Claims:- 1 TO 5	
(ii) ONLINE: WPI,	CLAIMS		

#### Categories of documents

<b>X</b> :	Document indicating lack of novelty or of inventive step.	P:	Document published on or after the declared priority date but before the filing date of the present application.
Y:	Document indicating lack of inventive step if combined with one or more other documents of the same category	E:	Patent document published on or after, but with priority date earlier than, the filing date of the present application.
A:	Document indicating technological background and/or state of the art.	&:	Member of the same patent family; corresponding

document.

Category	Identity of document and relevant passages	Relevant to claim(s)
<b>A</b>	WPI Abstract Accession No. 86-335260/51 and JP 61250/85 A (NICHIDEN ANELVA) see Abstract	

Databases: The UK Patent Office database comprises classified collections of GB. EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

Fig. 1

